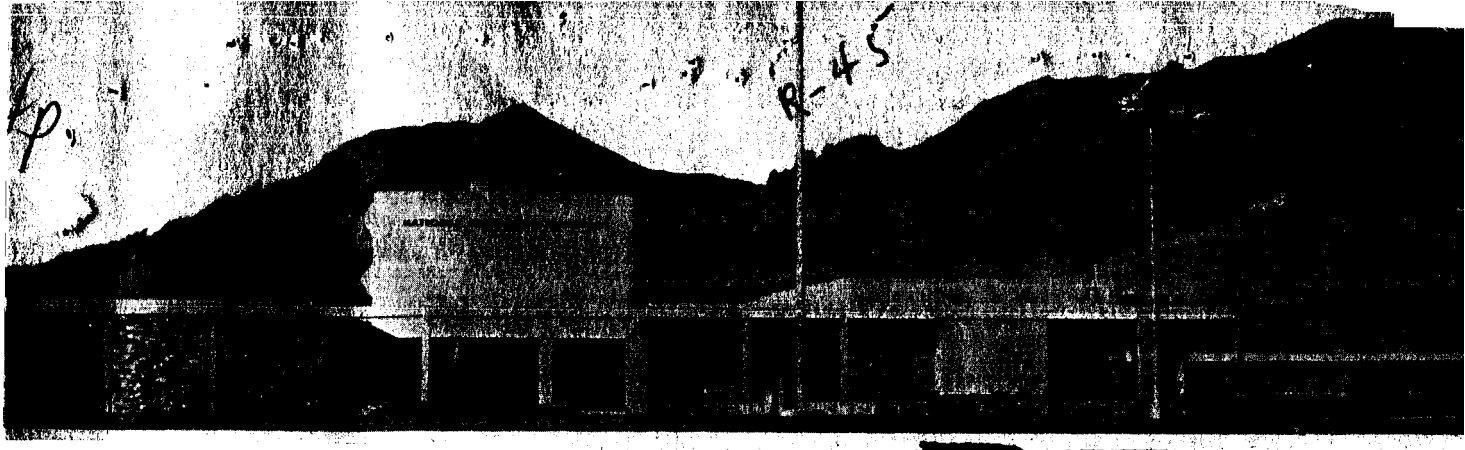

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THE SURFACE TENSION OF HYDROGEN

by

R. B. Stewart, F. E. E. Germann, R. D. McCarty

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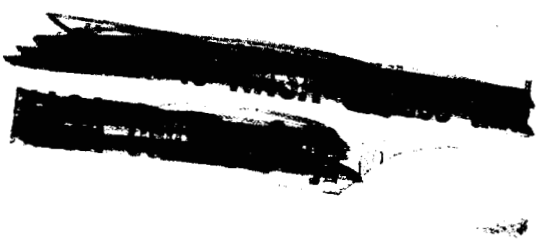

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THE SURFACE TENSION OF HYDROGEN

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ABSTRACT 13401

This preliminary report presents values of surface tension for normal hydrogen and parahydrogen for temperatures from 14° to 33°K. The basis for the calculation of these data is provided by a correlation of reduced surface tension data for helium-3, helium-4, normal hydrogen, and normal deuterium with reduced temperatures, and by the selection of a suitable relation for the variation of surface tension with temperature.

THE SURFACE TENSION OF HYDROGEN[1]

R. B. Stewart, F. E. E. Germann and R. D. McCarty

Introduction This report on the surface tension of hydrogen is issued as a preliminary report on a study of the experimental data for ten cryogenic fluids[2]. The study was undertaken to provide a basis for the selection of the most probable values for the surface tension data reported in the literature. Where the experimental data are limited to values for narrow ranges of temperatures, a functional relation was selected for the interpolation or extrapolation of the data to wider ranges of temperature.

Summary of the Literature on the Data for Hydrogen. The literature on the surface tension of hydrogen is not clearly definitive. The experimental data for normal hydrogen are listed in Table I and include eight values reported by Onnes and Kuypers [1][3] and two additional values by van Itterbeek [2]. All of the data are limited to temperatures between the triple point and the normal boiling point. The values reported by Onnes and Kuypers were subsequently corrected in a paper by van Urk, Keesom and Onnes [3] on the basis that the assumption of a circular meniscus made by Onnes and Kuypers was not as accurate as a graphical method by Verschaffelt [4], for determining the height of the meniscus. Van Itterbeek measured the surface tension of liquid hydrogen at two temperatures as a preliminary to his work on the surface tension of deuterium; he compared these values with the data as reported by Onnes and Kuypers and

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[1] A report on the surface tension of additional cryogenic fluids will be published at a later date.

[2] The surface tension of the following fluids were included: helium-3, helium-4, hydrogen, deuterium, neon, nitrogen, oxygen, carbon monoxide, argon, and methane.

[3] Numbers in brackets designate references in the bibliography at the end of the paper.

obtained satisfactory agreement. Van Itterbeek measured the height of the meniscus and found a large variation between his experimental values and the height as calculated from the Verschaffelt tables.

Because of the limited quantity of data and the lack of precision in the data, the evidence for the selection of the most probable values is inconclusive when comparisons are restricted to the hydrogen data alone. Therefore, in the absence of new experimental measurements, an additional basis for the selection of "best values" for the hydrogen data is provided by a comparison of the surface tension data for similar fluids.

Table I Surface Tension Data for Normal Hydrogen

Temperature (°K)	Surface Tension (dynes/cm)	Data Source
20.40	2.126	Onnes and Kuypers [1]
20.395	2.127	
20.39	2.130	
18.70	2.438	
17.99	2.575	
16.16	2.919	
14.685	3.167	
14.66	3.182	
20.40	1.910	van Urk, Keesom and Onnes[3]
18.70	2.1945	
17.99	2.3195	
16.16	2.631	
14.68	2.860	
20.32	2.19	van Itterbeek [2]
17.72	2.66	

Correlation of the Data for Surface Tension. A relation for the surface tension of fluids with simple molecules has been given as

$$\gamma = \gamma_o (1 - T/T_c)^n , \qquad (1)$$

where γ = surface tension, T = temperature, γ_o and n are constants, and T_c is the critical temperature. Guggenheim [5] demonstrated that a value of n = $^{11}/_{9}$ is adequate for neon, argon, nitrogen, and oxygen. Using this equation to represent the data for surface tension as a function of saturation temperature, values of n were determined by a least squares fit for the data of the several fluids included in this study. The results indicate a value of n = 1.0 to be satisfactory for helium-3, helium-4, hydrogen, and deuterium, while Guggenheim's value of approximately $^{11}/_{9}$ was confirmed for neon, nitrogen, oxygen, carbon monoxide, argon, and methane. The values of n as determined from a least squares fit of the experimental data for helium-3, helium-4, hydrogen, and deuterium are listed in Table II. In subsequent calculations, however, the value n = 1.0 was used for these fluids.

Table II Values of the Exponent n in Equation (1) from a Least squares Fit of the Experimental Data

Fluid	Experimenter	n
helium-3	Lovejoy [6]	1.124
	Zinov'eva [7]	0.992
	Esel'son and Bereznyak [8]	1.044
helium-4	Allen and Misener [9]	1.016
	van Urk Keesom and Onnes [3]	1.057
normal hydrogen	Onnes and Kuypers [1]	1.087
	van Itterbeek [2] (2 points)	1.057
	van Urk Keesom and Onnes [3] (using data from [1])	1.098
normal deuterium	van Itterbeek [2]	0.958

In evaluating the surface tension data for hydrogen, the data were further compared by the theory of corresponding states to the data for helium-3, helium-4, and deuterium. Following the suggestion of deBoer and Bird [10], the reduced surface tension was defined according to the theory of corresponding states for quantum mechanics, with the use of molecular parameters to account for

quantum effects which are particularly prominent in the surface tension of helium and hydrogen. The reduced values of surface tension and temperature are, $\gamma^* = \gamma\sigma^2/\epsilon$ and $T^* = kT/\epsilon$ respectively, where ϵ and σ are parameters for intermolecular potential functions and k is the Boltzmann constant. The values used are listed in Table III.

Table III Parameters for Reduced Temperature and Reduced Surface Tension*

Fluid	ϵ (ergs)	σ (ÅU)
helium-3	14.11×10^{-16}	2.556
helium-4	14.11×10^{-16}	2.556
normal hydrogen	48.60×10^{-16}	2.952
normal deuterium	50.70×10^{-16}	2.958

[$k = 1.3804 \times 10^{-16}$ ergs/°K]

* According to the theory of corresponding states for quantum mechanics

Equation (1) for the theory of corresponding states in quantum mechanics, with n = 1, becomes

$$\gamma^* = \gamma_o^*(1 - T^*/T_c^*). \qquad (2)$$

The coefficient γ_o^* in (2) for reduced surface tension may be roughly approximated as a function of the reduced critical temperature, T_c^*, by an empirical relation, $\gamma_o^* = A(T_c^*)^p$, as illustrated in Fig. 1. A least squares fit of the values of γ_o^* for the four fluids, where n = 1.0, indicated a best fit with A = 1.1706 and p = 2.102, whereas for fluids where n = $^{11}/_9$, A = 1.0 and p = 4.0. This approximation is not sufficient for the calculation of surface tension; however, the quantitative values for A and p do serve to illustrate further the differences in the characteristics of helium and hydrogen and their isotopes as compared to the other fluids. In addition, it was concluded that data for hydrogen, like helium, will extend along a straight line to the critical point.

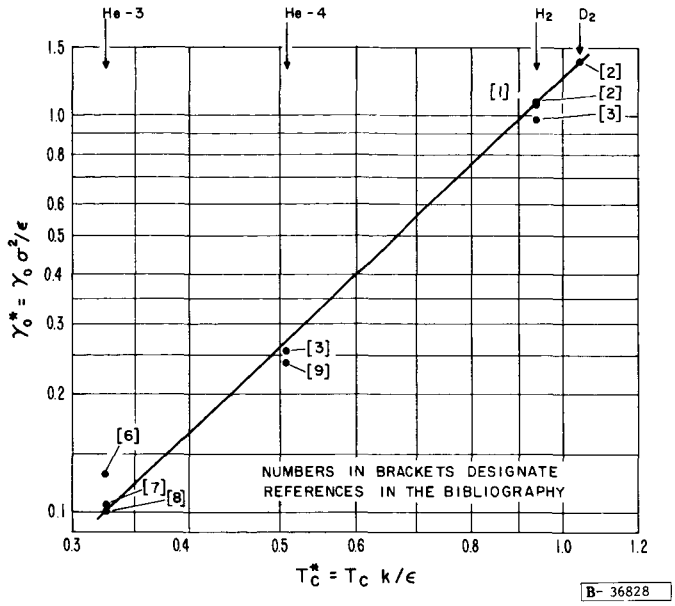

Fig. 1 Surface Tension Coefficients for Equation (2) for He-3, He-4, H_2, and D_2

Evaluation of the Surface Tension Data. As a result of the correlation illustrated in Fig. 1, the data selected as the "best values" for the four fluids were the data from the references listed in Table IV. These data are illustrated in Fig. 2 on reduced coordinates and are compared to the values calculated by (1) with n = 1 as represented by the straight line. The coefficients used for this calculation are listed in Table IV together with a summary of the deviations of the calculated surface tension from the experimental data selected for each fluid.

Table IV Summary of the Selected Data for Surface Tension

Fluid	Bibliography Reference of Selected Data	T_c (°K)	γ_o (dynes/cm)	Average Deviation of Selected Data from Equation (1)
Helium-3	[7] [8]	3.33	0.2185	1.21%
Helium-4	[3]	5.20	0.5308	2.59%
Normal Hydrogen	[1] [2]	33.19	5.6359	1.18%
Normal Deuterium	[2]	38.26	7.9653	0.37%

Equation (1) with n = 1 was used for the calculation of the smoothed values of surface tension for hydrogen tabulated in Table V from the lower temperature limit of the data to the critical point. It should be noted that the lowest temperature for which experimental data are available for hydrogen is close to the triple point and that the surface tension continues to be linearly dependent on temperature to this value. In the case of helium, however, the surface tension ceases to be linearly dependent on temperature at lower temperatures.

The smoothed values for parahydrogen in Table V were calculated, assuming γ_o to be the same as for normal hydrogen.

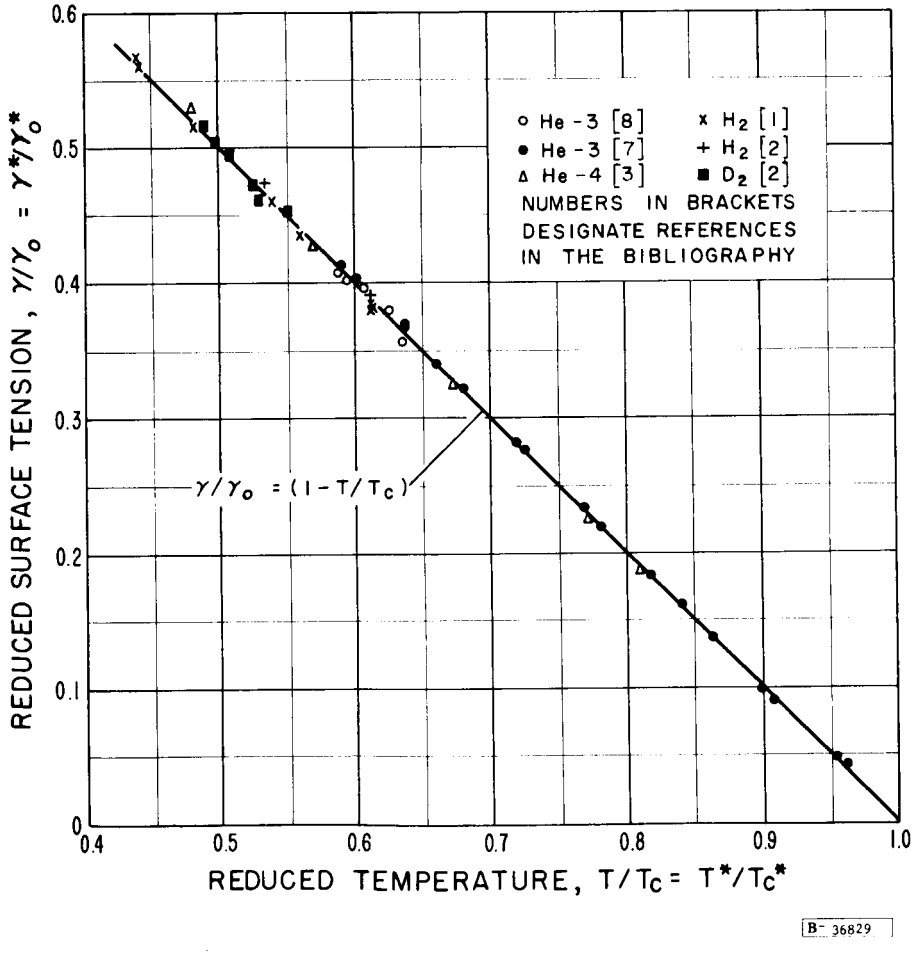

Fig. 2 Selected Data for Surface Tension for He-3, He-4, H_2, D_2

Table V Surface Tension of Normal Hydrogen and Parahydrogen [according to the equation $\gamma = 5.6359\ (1 - T/T_c)$]†

Temperature (°K)	Normal Hydrogen γ (dynes/cm)	Parahydrogen γ (dynes/cm)
14	3.259	3.244
15	3.089	3.073
16	2.919	2.902
17	2.749	2.731
18	2.579	2.560
19	2.410	2.389
20	2.240	2.219
21	2.070	2.048
22	1.900	1.877
23	1.730	1.706
24	1.561	1.535
25	1.391	1.364
26	1.221	1.193
27	1.051	1.022
28	0.881	0.852
29	0.711	0.681
30	0.542	0.510
31	0.372	0.339
32	0.202	0.168
33	0.032	-

† $\gamma_0 = 5.6359$ was determined from the data by [1] [2];
for normal hydrogen, $T_c = 33.19$°K,
for parahydrogen, $T_c = 32.98$°K.

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